DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 98

EFFECTS OF HEAT ON CELLULOID AND SIMILAR MATERIALS

BY

H. N. STOKES, Associate Chemist

and

H. C. P. WEBER, Assistant Chemist

Bureau of Standards

ISSUED OCTOBER 15, 1917

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By H. N. Stokes and H. C. P. Weber

CONTENTS

	Page
I. Introduction	3
II. General nature of materials	4
1. Composition	4
2. Uses	5
III. Decomposition by heat	5
IV. Combustibility	8
V. Experimental part	9
1. Samples tested	9
2. Method of analysis	10
3. Effect of heat	12
(a) Losses at 60° C	12
(b) Behavior at 100° C	13
(c) Decomposition at 110° C	15
(d) Decomposition at 135° C	21
(e) Gas evolved at 135° C	22
(f) Decomposition above 170° C (explosion test)	24
(g) Composition of the gases produced by decomposition	28
4. Combustibility	30
(a) Ignition point	30
(b) Rate of combustion	32
(c) Effect of continued heating below ignition point	33
(d) Effect of heat produced mechanically	37
(e) Extinguishing burning celluloid	38
VI. Conclusions	38
VII. Bibliography	40

I. INTRODUCTION

In 1907, at the request of the Steamboat-Inspection Service, the Bureau of Standards made a careful study of the literature of celluloid and other pyroxylin plastics and afterwards carried out an investigation of their properties with special reference to the hazard connected with their use and transportation. The results of the work are given in detail in this paper. In view of the present widespread interest in nitrocellulose products it seemed desirable to publish this paper, even though no account is taken in it of any advances that may have been made since 1908.

II. GENERAL NATURE OF MATERIALS

1. COMPOSITION

Pyroxylin plastics may be defined as solid solutions or mixtures of pyroxylin or a similar material with another substance, usually camphor. Unless colored or containing opaque matter they are nearly transparent. Under gentle heat, combined with pressure, they may be molded into any desired form. Pyroxylin is essentially the same as soluble or collodion cotton, a material which finds varied applications and which is the product of the limited action of a mixture of nitric and sulphuric acids on cellulose, usually in the form of cotton fiber or rag paper. It is chemically a mixture of cellulose trinitrates and tetranitrates, while the allied guncotton is essentially cellulose hexanitrate, $C_{12}H_{14}(NO_3)_6O_4$. The properties of pyroxylin differ in degree rather than in kind from those of guncotton, both being highly combustible and under suitable conditions explosive, while both if not suitably stabilized are subject to spontaneous decomposition.

Numerous attempts have been made to reduce the inflammability of pyroxylin plastics by incorporating the pyroxylin with other materials than camphor, but these do not appear to have met with any success. Furthermore the camphor is occasionally replaced by other materials, as acetanilide, in the so-called odorless celluloid. These modifications are relatively insignificant and it may therefore be stated that practically all pyroxylin plastics made at present consist of pyroxylin and camphor, either alone or incorporated with varying quantities of inert material, such as zinc oxide. The usual proportion is about two parts of pyroxylin to one part of camphor. While certain variations exist in the method of manufacture, some of which have to do with rendering the pyroxylin stable, it may be stated that, apart from the minute differences introduced in the stabilizing process, all pyroxylin plastics are essentially the same as far as chemical composition is concerned except for inert material.

As the term "celluloid" is, in universal popular use, applied to pyroxylin plastics, irrespective of their source, and as no other convenient word exists, it is employed in its popular sense in this paper. (In its legal sense the term "celluloid" applies only to the product of one American manufacturer.)

2. USES

Celluloid is a component of innumerable manufactured articles in a greater or less degree. The following is a list of a few of the more important articles composed wholly or in part of celluloid: Brushes, combs, soap boxes, mirrors, and other toilet articles, collars and cuffs, table cutlery, photographic films, dental plates, smokers' articles, piano keys, plumbers' hardware, billiard balls, blank books and stationery supplies, surgical instruments, toys, corsets, phonograph records, harness and automobile trimmings, mathematical and drafting instruments, hats, and shoe eyelets. Often the amount of celluloid is quite insignificant.

III. DECOMPOSITION BY HEAT

It is well known that guncotton and pyroxylin cotton, if not properly stabilized, are subject to spontaneous decomposition, which in some cases may be sudden or explosive. Whether celluloid, which contains about 65 per cent pyroxylin, ever undergoes decomposition at a temperature within the range of ordinary atmospheric variations does not seem to have been settled conclusively. Cases are on record of such decomposition, but these either date from a time when the handling of nitrocellulose was not as well understood as at present or on closer examination it does not appear certain that external causes may not have been at work, such as exposure to an undue amount of heat or, in the case of fires in celluloid works, to accidental ignition of the vapors of solvents. We have not been able to obtain any unimpeachable evidence that at normal or slightly elevated temperatures celluloid ever takes fire spontaneously. In a later section of this paper are given several series of experiments which indicate that at 60° C (140° F) celluloid loses weight very slowly through volatilization of camphor and residual traces of solvent, but that at 100° C (212° F) the loss is much more rapid and is accompanied by decomposition of the pyroxylin itself.

The fact that pyroxylin and guncotton can be brought to explode is a sufficient indication that the decomposition is exothermic—that is, that heat is evolved, not absorbed, during the decomposition. There is no reason for supposing that this exothermic property will be changed by mixing with another substance, and, in fact, it is easy to prove that it is not changed. In experiments described in a later section it is shown that celluloid, if so insulated as to retain the heat and exposed to a tempera-

ture of about 135° C (275° F) attains a higher temperature[1] quite rapidly. This is because heat is evolved during the decomposition and is prevented from escaping. The more perfectly the heat is kept in the more quickly the temperature rises, until the celluloid finally reaches the point of sudden decomposition. The decomposition of celluloid is, therefore, different from that of materials like wood, cotton, etc., in that it is accompanied by noticeable evolution of heat and that if this heat is kept from escaping the temperature rises continuously.

Celluloid does not contain enough oxygen for its complete combustion, nor, in fact, enough to convert it entirely into permanent gas, but the heat is sufficient, if suddenly liberated, to volatilize it, with the exception of a trifling residue of carbon. It has been abundantly shown by others, and we have constantly observed, that if celluloid is raised to a certain temperature, it suddenly decomposes or "goes up in smoke." While this decomposition is not explosive in the sense that it is directly able to shatter objects with which it is in contact, it is nevertheless closely analogous to true explosion, and the large volume of gas produced is able to burst its container or to explode if mixed with air. If a piece of celluloid, open to the air, is touched with a hot wire, decomposition occurs at the point of contact but does not usually spread unless ignition ensues. This is because the heat of decomposition is conducted or radiated away too rapidly. If, however, the celluloid is kept in a confined space, the decomposition spreads rapidly. If strips of celluloid are placed in a long glass tube closed with a perforated stopper, and the upper part of the tube is warmed at one point until decomposition starts in one spot, this spreads rapidly down the entire length of the tube and torrents of inflammable gas are given off. If a hot object is dropped into a box of celluloid and the lid is instantly replaced, the reaction spreads rapidly through the entire mass and is in no wise interfered with by plunging the box under water. From this it is obvious that it would be very difficult to check the decomposition of a mass of packed celluloid by means of water, and the more careful the packing the more difficult it is to check. When celluloid is in thin sheets and loosely packed, however, it is not difficult to check its decomposition because, on account of the more ready access to water, the material is quickly cooled below the temperature at which the reaction can proceed.

[1] This effect is noticeable even at lower temperatures, but at 135° C this becomes quite marked without providing particularly effective heat insulation. In the experiments with the "steam coil," described later on, the initial temperature was much lower, but the material was well insulated.

In a later section of this paper are described experiments in which a mass of wrapped celluloid was heated by a steam coil, the temperature of which did not exceed 120° C (248° F). The temperature in the interior of the mass rose gradually above that of the steam coil until sudden decomposition occurred, the whole mass of material being converted into suffocating and inflammable gas in a few moments. In some cases the escaping gas ignited (no flame being in the vicinity), while in every case the cotton wrapping was found to be glowing, and access to the air was sufficient to start a flame. What the resultant temperature was can only be surmised, but it was at least sufficient to melt the lead steam coil, even through the thick cotton wrapping.

It is also shown that celluloid heated in a box at 135° C (275° F) decomposed with a flash, and that the pressure of the exploding gases, in a relatively large space, was sufficiently great to burst open the door and bend at right angles the brass latch, which was 2 mm thick.

To repeat, there appears to be no good evidence that pyroxylin plastics often inflame spontaneously or that they are directly explosive under any conditions. They present a marked analogy with explosives in that they undergo at an elevated temperature a very rapid and, under certain circumstances, entirely uncontrollable decomposition. The exact point at which this occurs is of secondary importance, because it is the culmination of a process of slow decomposition which begins at a much lower temperature and which proceeds the more rapidly the more perfect the retention of heat through packing and insulation. It is equally impossible to fix a point at which this process of slow decomposition becomes dangerous, as this also depends on the degree of insulation. It is sufficient to say that the best material we have been able to obtain can be brought to the sudden decomposition point if kept in an environment of 120° C (248° F), while with more perfect insulation, or in larger masses, it might decompose at lower temperatures. The above is a temperature to which it might easily be exposed in the case of a fire in the same room, without being in contact with it. The result of this decomposition is the sudden evolution of large volumes of hot gas which, on coming into contact with the air, are likely to ignite of themselves, or if not, then to form a highly explosive mixture, which will contain large but varying quantities of carbon monoxide and oxides of nitrogen, both of which are poisonous and the latter very suffocating.

IV. COMBUSTIBILITY

The term "combustibility" may mean either the ease with which combustion is started or the rate at which it proceeds after starting. As is well known, these are entirely different things. The definition of the ignition temperature is uncertain, as in the case of materials which give off combustible gas on heating; the ignition temperature is that of a mixture of the gas with varying amounts of air, rather than of the solid itself. In this respect celluloid resembles wood, but the temperature of decomposition is much lower than that of wood, as is also the ease with which it may be ignited. It is not possible to set fire to a pine board by holding a match to its upper surface, yet we have frequently easily and permanently ignited a heavy plate of celluloid, one-half inch thick, by holding a burning match to its upper surface. It is possible to ignite a plate of sealing wax in the same way, but unlike celluloid the flame does not spread and dies out in a few moments.

If by "combustibility" is meant the rate at which a flame once started is propagated, then it is shown by the results of our experiments that a thin stick of celluloid is five to ten times as combustible as a wooden stick of the same size under the same conditions. We soon reach the limit of size of a wooden stick which can readily be ignited and which will continue to burn if held horizontally, while an even larger stick of celluloid will burn easily.

In any sense, therefore, celluloid is much more combustible than wood under similar conditions, and the flame is not as easily extinguished. It is not the celluloid which burns, but the gas evolved from it, just as is the case with other materials burning with flame. While wood has to be heated either from without or by its own combustion to cause it to give out inflammable gas, celluloid, if in a confined space, generates by itself enough heat to support a decomposition once started, entirely apart from actual combustion. It is therefore impossible to stop the progress of decomposition by shutting off the air, and inflammable gas will continue to be generated. Celluloid has been ignited with no greater initial source of heat than an air bath at 135° C (275° F) and has been caused to set fire to cotton and to its own gas, using no source of heat other than a steam coil at 120° C (248° F).

It should be distinctly understood that this Bureau is not expressing the opinion that "celluloid" and pyroxylin plastics in general constitute an unusual source of danger in use. It would

be no more just to condemn them in this connection than it would be to warn the public against the use of petroleum, of cotton fabrics, and the like. It is, however, right that the very inflammable nature of these materials should be known, as they fill a very important place, and it can only be urged that the same intelligence be used in handling them as is used in handling other highly combustible materials which are to be found in every house or which are worn on the person.

There was found to be no essential difference in composition and behavior between the products of the two American firms whose material was examined or between these and goods of foreign manufacture. Some samples are more stable than others, but this has no connection with the source. We therefore regard the different makes of pyroxylin plastics that were obtainable in 1908, so far as we have examined them, as on the average equally safe, or unsafe, as the case may be.

V. EXPERIMENTAL PART

1. SAMPLES TESTED

In this report the names of the manufacturers have not been indicated. The materials were obtained in part directly from the makers for experimental purposes and in part were purchased in the open market. The latter samples consisted of miscellaneous articles of unknown origin and articles, largely toys of French and German make, the origin of which was guaranteed by the dealer. Those groups have been designated as follows:

Samples 1–29: Material submitted by one large American manufacturer.

Samples 41–56: Origin of material not known.

Samples 61–67: French material.

Samples 71–81: German material.

Samples 101–119: Material submitted by another large American manufacturer.

The samples examined consisted of plates 0.15 to 13 mm thick, such as are used by the manufacturer in the preparation of trade articles, or of manufactured articles of all kinds, such as toys, combs, brushes, collars, etc. The approximate composition of a number of the samples was found to be as shown in Table 1.

104996°—17——2

TABLE 1

Approximate Composition of Some Pyroxylin Plastics

Sample	Nitrocellulose	Ash	Camphor and solvent by difference	Sample	Nitrocellulose	Ash	Camphor and solvent by difference
	Per cent	Per cent	Per cent		Per cent	Per cent	Per cent
1A		21.47		7	71.6	6.45	21.9
2A		.99		8	68.8	4.29	26.9
3A		16.70		9	72.9	1.00	26.1
4A		1.82		10	75.0	3.44	21.6
5A		6.77		11	68.6	5.36	26.0
6A		3.78		64	78.0	2.09	19.1
7A		3.65		101	77.1	.68	22.2
1	71.4	1.66	26.94	102	68.0	.82	31.2
2	67.5	1.12	31.38	103	60.0	19.56	20.4
3 [a]	43.4	21.19	19.4	104	58.0	18.40	23.6
4 [a]	43.2	20.50	20.3	105	65.4	4.59	30.0
5	75.0	1.70	23.3	111	73.0	1.44	25.6
6	73.4	4.97	21.6	114	54.6	28.00	17.4

[a] This sample also contained 16 per cent cloth.

2. METHOD OF ANALYSIS

In the analyses given the nitrocellulose was determined directly. The celluloid was dissolved in acetone acidified with nitric acid, which caused the zinc oxide to go into solution with the nitrocellulose. The nitrocellulose was then precipitated by pouring the solution into water containing a small percentage of ammonium nitrate, the nitrocellulose being obtained in better condition for subsequent manipulation under these conditions. In order to remove dyes and camphor as completely as possible, the nitrocellulose was dried, redissolved, and again precipitated. The ash, which was also determined directly, consisted essentially of zinc oxide in all cases where mineral matter had been added to the material. Unloaded samples contained about 1 per cent of ash, which was in all probability present in the materials from which the celluloid was prepared. Materials such as celluloid collars and cuffs and the sheets from which these articles are manufactured contain an inner layer of cloth with the celluloid mixture spread on both sides.

The values given under camphor are obtained by difference and include besides this the small percentage of solvent left from the manufacture and oils or other substances added intentionally. The question of whether there was camphor or a camphor substitute used in the celluloid was not entered into. In the majority of the cases camphor was evidently the material added

to the nitrocellulose. The celluloid as bought on the market contains a small percentage of the solvent which was used during the process of manufacture. This was shown by the behavior of the samples in a vacuum. When heated in an evacuated tube to temperatures slightly above the ordinary, small quantities of liquid, together with camphor, distilled into the cooler portion of the tube. This liquid, in many cases, possessed the characteristic odor of amyl acetate. Various samples of celluloid when left in a vacuum desiccator for 11 days showed the losses given in Table 2 and Fig. 1.

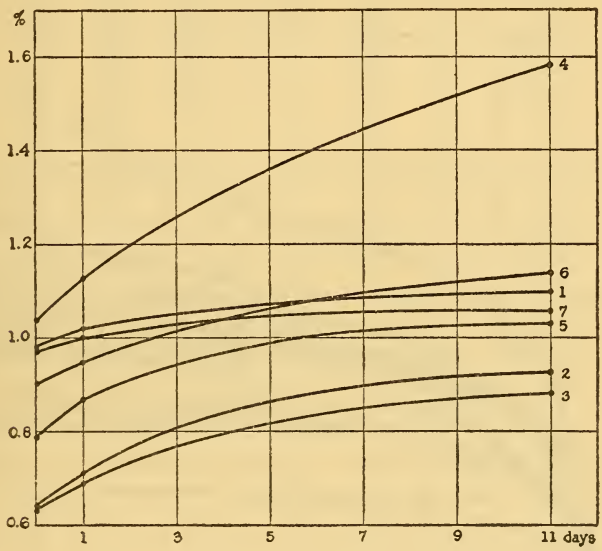

FIG. 1.—*Percentage loss in weight in vacuum*

TABLE 2

Percentage Losses in Weight in Vacuum Desiccator

Sample	1	2	3	4	5	6	7
Loss	1.10	0.94	0.88	1.59	1.04	1.14	1.15

This loss is probably due to surface moisture and solvent. The question whether there is any decomposition with evolution of gases was answered in the negative from the following experiment:

Two samples of celluloid were inclosed in glass tubes, which were then evacuated to a pressure of 0.01 mm of mercury. After standing a week they were again pumped out and not more than 0.1 cc of gas was obtained. Upon repeating, a small but negligible amount of gas was again obtained.

3. EFFECT OF HEAT

(*a*) *Losses at 60° C (140° F)*.—Eleven samples of celluloid were heated to 60° C in a thermostat for a period of 10 days. Each sample consisted of six or seven small sheets about 3 by 4 cm wrapped together with a sheet of tissue paper between each. This was done to make the test comparable with the ordinary conditions of packed celluloid. The temperature of the thermo-

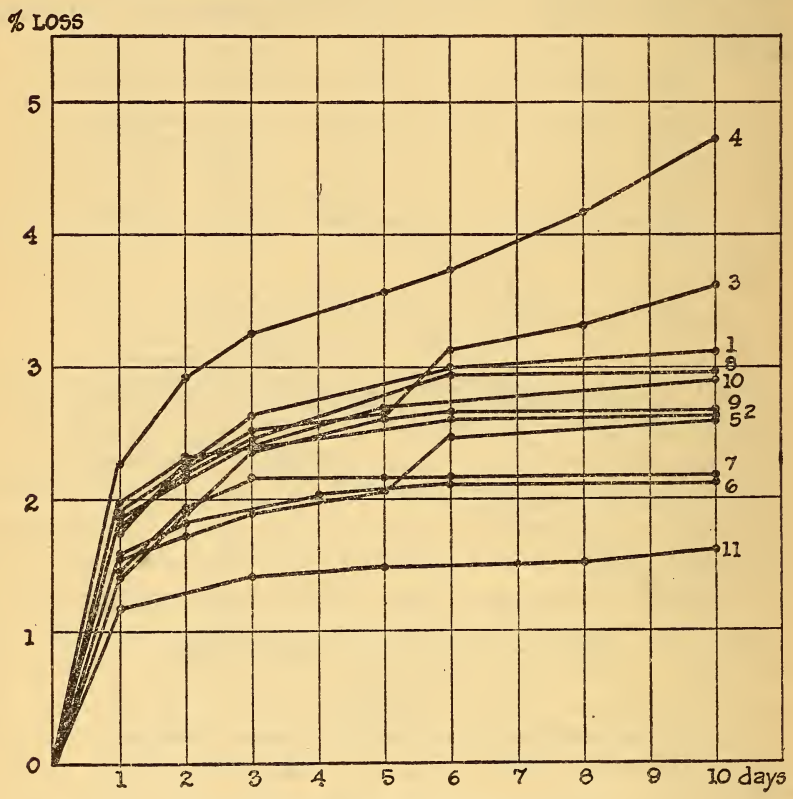

FIG. 2.—*Percentage loss in weight at 60° C*

stat was kept constant by means of a gas regulator. The losses given in Table 3 are shown graphically in Fig. 2.

As will be seen, the greatest losses occurred during the first 24 hours. After about six days the loss reached a total of between 2 and 3 per cent for the majority of the samples and showed no further increase. The samples showed very little evidence of change, the wrappings not having been affected and the articles having retained their original appearance.

TABLE 3

Percentage Loss in Weight at 60° C

Sample	Weight of sample	1 day	2 days	3 days	5 days	6 days	8 days	10 days
	g							
1	5.70	1.75	2.28	2.63	.....	2.98	.....	3.1
2	11.71	1.54	1.71	1.88	2.05	2.48	.....	2.6
3	8.28	1.92	2.27	2.52	2.63	3.12	3.3	3.6
4	6.14	2.27	2.92	3.25	3.57	3.73	4.2	4.7
5	3.06	1.95	2.28	.....	.....	2.59	.....	2.59
6	3.80	1.57	1.83	.....	.....	2.10	.....	2.10
7	4.15	1.45	1.93	2.17	.....	.....	.....	2.17
8	4.06	1.72	2.21	2.46	.....	2.94	.....	2.94
9	4.20	1.43	1.90	2.38	.....	2.62	.....	2.62
10	3.74	1.87	2.14	2.40	.....	2.67	.....	2.90
11	16.18	1.17	1.30	1.42	1.48	.....	1.50	1.60

(*b*) *Behavior at 100° C (212° F)*.—Upon heating celluloid in an evacuated tube to 100° C the greater part of the camphor was distilled off and condensed in the cooled portion of the tube, together with some solvent. In the course of several hours camphor to the extent of 5 to 10 per cent of the weight of the total celluloid distilled over. It was not possible to carry the distillation further than this, owing to the fact that the pressure in the tube increased on account of the decomposition of the celluloid.

The treatment described under (*a*) was carried out with samples at 100° C instead of 60° C. The samples 1–11 were from the same pieces as in the previous test and were cut into sheets and wrapped in paper.

The losses in weight from day to day were noted for 10 days. The results are given in Table 4 and Fig. 3.

TABLE 4

Percentage Loss in Weight at 100° C

Sample	Weight of sample	1 day	2 days	3 days	4 days	5 days	6 days	10 days
	g							
1	5.71	4.91	6.31	7.11	8.06	9.1	9.8	14.0
2	11.64	4.16	4.72	4.98	5.15	5.6	6.1	9.4
3	7.92	6.19	7.45	8.59	9.22	10.1	11.2	20.2
4	5.96	9.06	10.40	11.41	12.58	14.1	15.8	21.8
5	2.91	6.87	11.00	16.84	24.10	29.2	32.3	39.2
6	3.81	9.71	13.63	17.36	21.52	26.0	28.9	36.0
7	4.16	6.25	9.13	12.47	18.02	23.1	27.4	36.8
8	4.01	19.95	23.18	27.17	30.43	32.9	34.4	38.9
9	4.23	5.91	7.33	8.27	11.58	16.5	20.8	35.0
10	3.77	5.83	8.22	10.60	14.58	18.8	22.0	33.7
11	15.88	5.67	6.99	8.12	9.51	10.8	12.3	13.4

The graphic representation shows a fairly constant loss after the first day, which varies widely, however, for different samples of celluloid, the lowest total loss being 9.4 per cent and the highest 39.2 per cent. In a number of cases the paper wrapping became charred the first day. At the end of the test the wrapping material was strongly decomposed, partially charred, the remainder yellow and brittle, so that it could be rubbed to a powder. Those samples of celluloid that showed the greatest losses had swelled up enormously, forming bloated, spongy masses. The celluloid

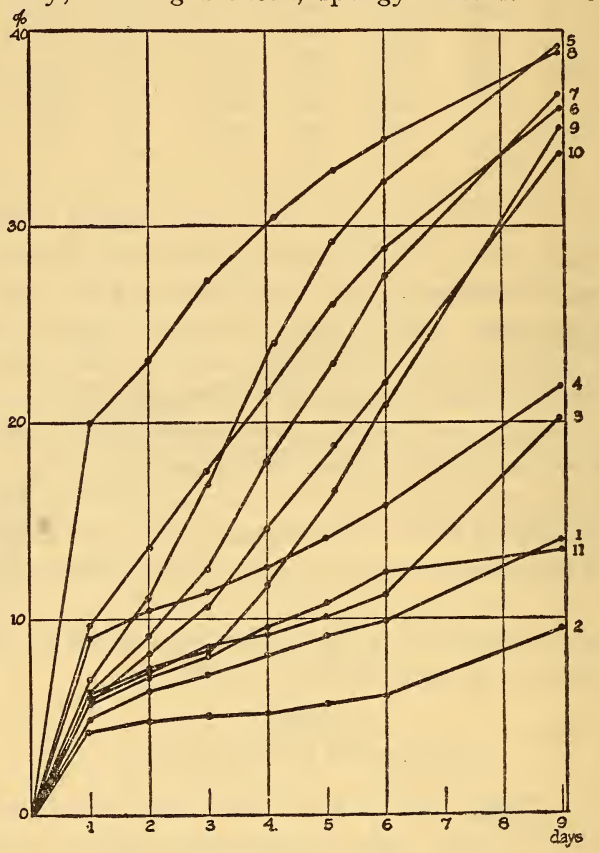

FIG. 3.—*Percentage loss in weight at 110° C*

itself had become brittle and easy to powder, the dyestuffs used having been also entirely decomposed. The camphor content and the losses are shown here for comparison.

This comparison shows that upon heating the total loss in weight in most cases was in excess of the content of camphor. Assuming that all the camphor was driven off, there still remains a loss of 1 to 16 per cent due to decomposition. That all the camphor was not volatilized is, on the other hand, shown conclusively by samples 1, 2, and 11.

TABLE 5

Comparison of Camphor Content and Loss on Heating to 100° C

Sample	1	2	3	4	5	6	7	8	9	10	11
Loss	14.00	19.40	20.2	21.8	39.2	36.0	36.8	38.9	35.0	33.7	13.4
Camphor	26.94	31.38	19.4	20.3	23.3	21.6	21.9	26.9	26.1	21.6	26.0
Excess	.....	.....	.8	1.5	15.9	14.4	14.9	12.0	8.9	12.1	.....

(*c*) *Decomposition at 110° C (230° F)*.[2]—A number of samples of celluloid were heated in a thermostat at 110° C for eight days. Another set of samples was subjected to the same treatment for 10 days. The details of this test differed from the preceding one in several points. The samples were not wrapped, but consisted of sheets weighing 5 or 10 g each and loosely rolled into bundles. The thermostat was an electrically heated oven with automatic temperature regulation. Constant circulation of the air in the interior of the thermostat was maintained by means of an electrically driven fan. The results obtained with this arrangement were as follows:

TABLE 6

Percentage Losses in Weight at 110° C

EXPERIMENT A

Sample	1 day	2 days	3 days	4 days	5 days	6 days	7 days	8 days	9 days	10 days
1	4.8	6.5	6.6	7.0	9.0	9.2	10.7	11.6	.....	.....
2	3.6	4.8	5.2	5.9	6.9	7.9	10.4	13.0	.....	.....
3	5.8	7.3	9.6	12.0	14.7	16.7	19.2	20.7	.....	.....
4	7.8	9.0	10.7	13.0	14.9	17.1	19.4	20.1	.....	.....
5	5.4	6.9	9.1	11.9	13.1	14.0	19.0	23.8	.....	.....
6	8.6	20.5	22.3	25.6	27.5	28.9	32.5	34.4	.....	.....
7	3.2	4.5	5.8	7.8	11.2	15.0	19.2	22.6	.....	.....
8	3.8	8.3	13.6	18.2	21.3	23.8	28.0	30.2	.....	.....
9	3.0	3.9	5.0	6.9	9.0	13.7	17.5	21.6	.....	.....
10	2.9	3.7	4.8	6.4	6.8	7.4	9.7	11.6	.....	.....
11	1.6	3.0	8.8	12.4	15.9	17.9	20.2	23.3	.....	.....

EXPERIMENT B

101	5.2	6.5	.....	7.5	.....	28.0	31.0	42.0	43.3	44.5
102	8.7	10.9	11.8	13.3	.....	35.0	41.5	43.5	44.8	45.7
103	3.5	4.5	5.3	5.9	.....	8.0	9.5	10.8	12.0	13.1
104	8.5	10.5	11.1	11.7	.....	12.8	14.0	14.8	16.0	16.4
109	7.0	12.4	16.0	18.4	.....	22.8	25.8	27.4	28.6	29.6
111	4.5	6.0	6.7	8.8	.....	35.3	39.0	40.4	41.7	42.2
114	4.3	4.9	.....	5.82	.....	6.4	7.18	7.76	8.54	8.74
115	2.7	3.4	3.9	4.4	.....	5.57	6.88	7.86	8.52	8.7
119	7.0	8.5	9.2	9.6	.....	11.0	12.0	12.8	14.0	14.2
130	6.4	7.6	7.8	8.2	.....	8.6	9.0	9.4	9.4	9.4

[2] Sy. J. Amer. Chem. Soc., 25, p. 549, 1903; "A good nitrocellulose should not lose more than 8 per cent in six 8-hour days" at 115° C. Escales. Z. angew. Chem., 18, p. 946, 1905; on 40 nitrocellulose powders in six days of 24 hours each at 110° C, the highest loss was 25.64 per cent, lowest 4.32 per cent; average of 39 samples was 8.77 per cent.

A remarkable fact appears from this set of experiments. Comparing the results with those obtained from the wrapped samples it appears that, for the same period of heating, the unwrapped samples at 110° lost less than the wrapped samples at 100°. It is not necessary to seek far for an explanation of this phenomenon. Willcox [3] showed that the rate of decomposition of nitrocellulose

FIG. 4.—*Percentage losses in weight at 110° C. Samples 1 to 11*

depends upon whether the gaseous products remain in contact with the decomposing substance or not. If the decomposition products are not removed, the rate is accelerated. In succeeding experiments it will be shown that by insulating celluloid against loss of heat by conduction the temperature of the mass rises above that of the surroundings, the amount of rise depending upon the perfection of the insulation. The reaction is strongly exothermic, and,

[3] J. Amer. Chem. Soc., 30, p. 271; 1908.

celluloid being a poor conductor of heat, the action under these conditions is cumulative.

In Figs. 4 and 5 the results have been plotted in graphic form, with percentage losses in weight as ordinates and times as abscissas. In Fig. 6 are plotted the average losses for each of two sets of samples from two manufacturers, as well as the combined average.

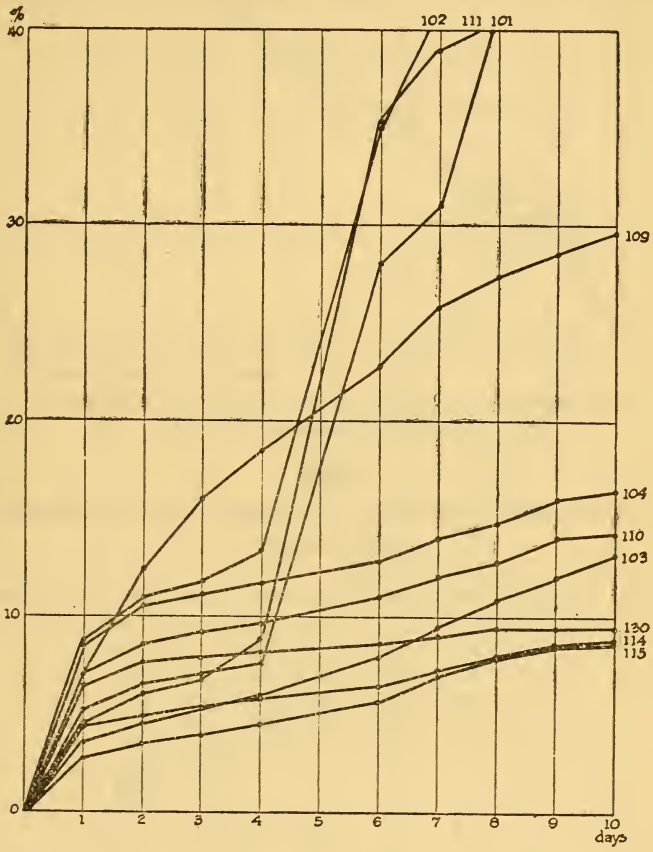

FIG. 5.—*Percentage losses in weight at 110° C. Samples 101 to 130*

It will be seen that, as far as this test is concerned, the stability of the average sample is about the same in each case.

In Table 7 the losses are calculated to the ash-free sample; that is, referring the losses to the amount of camphor and nitrocellulose present, which two constituents furnish the volatile components to which the losses in weight from decomposition may be ascribed.

104996°—17——3

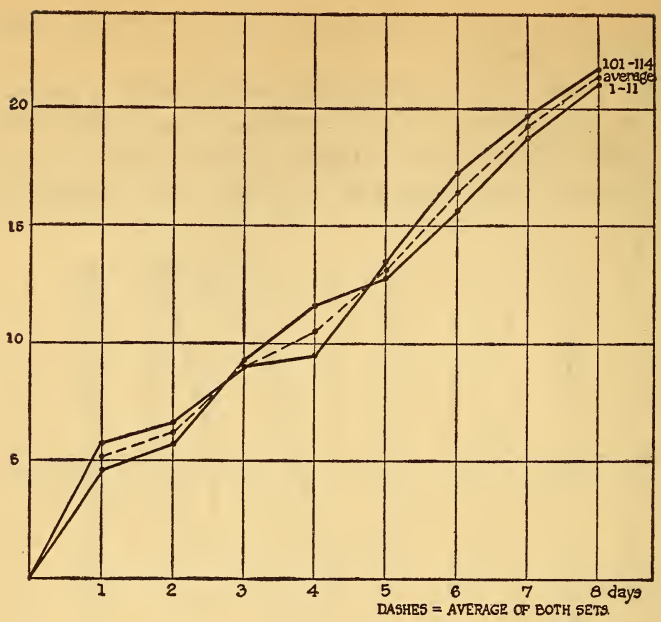

FIG. 6.—*Average percentage losses for two sets of samples at 110° C, and combined average of the two*

TABLE 7

Losses at 110° Calculated as Percentage of Ash-Free Weight

EXPERIMENT A

Sample	1 day	2 days	3 days	4 days	5 days	6 days	7 days	8 days	9 days	10 days
1	4.88	6.61	6.71	7.12	9.15	9.36	10.88	11.8	.....	.....
2	3.64	4.86	5.26	5.97	6.98	7.99	10.5	13.15	.....	.....
3	9.22	11.64	15.27	19.09	23.4	26.58	30.5	32.99	.....	.....
4	12.3	14.2	16.85	20.48	23.47	26.93	30.55	31.65	.....	.....
5	5.5	7.02	9.3	12.1	13.3	14.2	19.3	24.2	.....	.....
6	9.05	21.6	23.5	27.0	29.0	30.4	34.2	36.2	.....	.....
7	3.4	4.8	6.2	8.3	12.0	16.0	20.5	24.2	.....	.....
8	4.0	8.7	14.2	19.0	22.25	24.9	29.3	31.6	.....	.....
9	3.2	4.0	5.2	7.15	9.3	14.2	18.1	22.4	.....	.....
10	2.9	3.7	4.8	6.5	6.9	7.5	9.8	11.7	.....	.....
11	1.7	3.2	9.3	13.1	16.8	18.9	21.4	24.6	.....	.....
EXPERIMENT B										
101	5.2	6.6	.....	7.6	.....	28.2	31.2	42.3	43.6	44.8
102	8.8	11.0	11.9	13.4	.....	35.3	41.8	43.9	45.2	46.0
103	4.4	5.6	6.6	7.3	.....	10.0	11.8	13.4	14.9	16.3
104	10.4	12.9	13.6	14.3	.....	15.7	17.2	18.1	19.6	20.1
109	7.1	8.7	16.4	18.9	.....	23.6	26.4	28.1	29.3	30.4
111	4.6	6.1	6.8	8.9	.....	35.8	39.6	41.0	42.3	42.8
114	6.0	6.8	7.4	8.1	.....	8.9	10.0	10.8	11.9	12.1
119	9.0	10.8	11.8	12.5	.....	14.1	15.4	16.4	17.8	18.3
130	9.0	10.8	11.4	11.7	.....	11.4	12.9	13.4	13.4	13.4

From the graphic representation of the results for the first set of samples (Fig. 7) it will be seen that the relative rate of decomposition was greatest in those samples containing the largest percentage of mineral matter, in this case zinc oxide, and least in those samples containing the lowest percentage of mineral matter. The 11 samples tested consisted of sheets of celluloid furnished by the manufacturer. The samples were from the same firm and had

FIG. 7.—*Percentage losses in weight at 110° C, calculated to ash-free material. Samples 1 to 11*

apparently undergone the same processes. For the sake of a rough comparison they may be considered in three groups. The first comprises three samples with an average ash content of 1.25 per cent and loss of 12 per cent; the second, four samples with an average ash content of 4.3 per cent and an average loss of 24 per cent, while the third group comprises four samples with an average ash content of 12.8 per cent and an average loss of 33 per cent.

The mineral constituent in all these cases was zinc oxide. The percentages are for losses in eight days referred to ash-free material.

One of two explanations may be ventured to account for this peculiarity. Either a nitrocellulose of a lower degree of stability has been used in the manufacture of these articles containing large quantities of filler or there is a direct action attributable to the

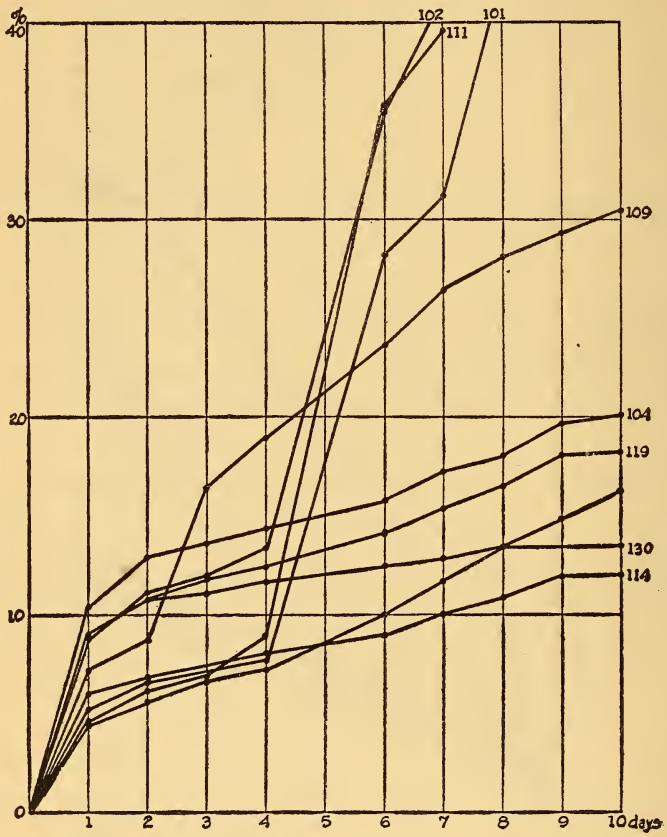

FIG. 8.—*Percentage losses in weight at 110° C, calculated to ash-free material. Samples 101 to 130*

zinc oxide, causing an increase in the rate of decomposition. In the second set of samples this relation is not shown in the same way. (See Fig. 8.)

There is here, at the end of the eight-day period, one group of three samples with an average ash content of 1 per cent and an average loss of 42.8 per cent.[4] These samples are evidently anomalous, on account of both the very extended decomposition

[4] These curves are not shown to their end in the plate on account of lack of space.

which they have undergone and the abrupt change of the rate of decomposition after the fourth day. The lower group of five samples contained 23.6 per cent of ash and showed a loss of 14.4 per cent on the average.

On the whole, these results do not show that the addition of zinc oxide increases the stability of nitrocellulose in celluloid articles in the sense of decreasing its rate of decomposition. It may mask the decomposition for a time. What rôle the zinc oxide plays under these conditions was not determined. In the case of the hydrolysis of an ester the addition of a basic component to the system would be expected to accelerate the reaction. Whether or not the reabsorption of the decomposition gases noted under the Mittasch test, given further on, has any connection with this is not certain. The effect of the addition of basic substances to nitrocellulose has been touched upon by various observers.

Mittasch [5] studied the effect of various additions on the amount of gas evolved by nitrocellulose when heated to 135°. The curves for nitrocellulose with additions of sodium carbonate show a decided increase and with calcium carbonate a very slight increase. Magnesium oxide caused a decrease at first, but the curve showing the evolution of gas soon crosses that of the pure nitrocellulose and then shows a decided increase. Ignited marble caused a smaller amount of gas to be given off, but in this experiment a reabsorption of the gases was observed during the first eight hours of the experiment. Bergmann and Junk [6] found that the evolution of gases by nitrocellulose heated for two hours at 132° is decreased by the addition of small amounts of sodium carbonate. If the sodium carbonate is, however, intimately mixed with a stable nitrocellulose, the amount of gas evolved is largely increased.

(*d*) *Decomposition at 135° C (275° F)*.—A number of samples weighing from 2 to 5 g were next kept in the thermostat at 135°. Each sample was in a small glass beaker of about 150 cc capacity. The fan in the thermostat was kept in motion during the experiment. Of 20 samples, including celluloid in sheets and manufactured articles such as combs, collars, rattles, soap boxes, dice, etc., more than two-thirds ignited or exploded in less than two hours. The force of the decomposition was considerable and was in a number of instances accompanied by a flash of flame. The thermostat, which was the same as that used in the preceding tests, had a volume of about 28 liters. The front side consisted

[5] Z. angew. Chem., 16, pp. 936–939; 1903.

[6] Z. angew. Chem., 17, p. 1022; 1904.

of a door with a glass window consisting of a double plate of glass. The door was closed by means of a catch of brass about 1 cm wide, 2 cm long, and about 2 mm thick. In one instance the door was burst open and the catch was found to have been bent at right angles. In several other instances the heat generated was sufficient to melt the solder of the revolving fan, causing it to fall to pieces. In no case was there any flame in the vicinity to ignite the gas mixture. As far as could be observed the way in which the explosion took place was as follows:

The sample gradually puffed up until it was enormously swelled. Suddenly the outer covering of this mass would burst, sending out large volumes of dense fumes, and in an instant the whole mass was in decomposition. In a number of cases this decomposition followed with explosive rapidity accompanied by a flash of flame, the substance burning up practically without organic residue.

(*e*) *Gas Evolved at 135° C (275° F)*.—Mittasch uses a method for the determination of the stability of nitrocellulose in which the sample is heated to 135° for a specified time and the evolved gases are collected and measured. This test was applied to celluloid for the purpose of determining whether an essential difference between the various celluloids could be found. The manipulation of the test was as follows:

Two grams of the celluloid was weighed and inserted in a glass tube having a ground-glass cap and delivery tube. This was suspended in a second apparatus in such a manner that it was exposed to the vapors of boiling amyl alcohol, to which enough fusel oil had been added to depress the boiling point to 135°. A thermometer, inserted alongside on the tube, allowed the temperature to be read. The delivery tube for the gases dipped under mercury. The tube was allowed to assume the temperature of the bath and the expanding gas allowed to escape until the tube had attained the temperature of the bath, after which the delivery tube was slipped under the eudiometer and the evolved gases were collected, and the volume was noted from time to time.[7] The results are shown graphically in Fig. 9.

In general, the samples are here arranged in the same order as in the other tests, loss of weight, ignition, etc., the samples 5 and 6 showing up poorly as compared with the remainder. Here, again, it is to be noticed that those samples having the greatest amount of mineral matter do not by any means give the smallest volume of

[7] Bergmann and Junk stated (Z. angew. Chem., 17, p. 984; 1904) that good nitrocellulose should give off not more than 2.5 cc of nitric acid when heated for two hours.

gas. One remarkable fact was brought out. In a number of samples there was an absorption of gas noticeable after decomposition had once set in. This reabsorption continued for from 15 minutes to an hour. It was shown by the fact that after a very slight amount of gas had been driven over into the eudiometer

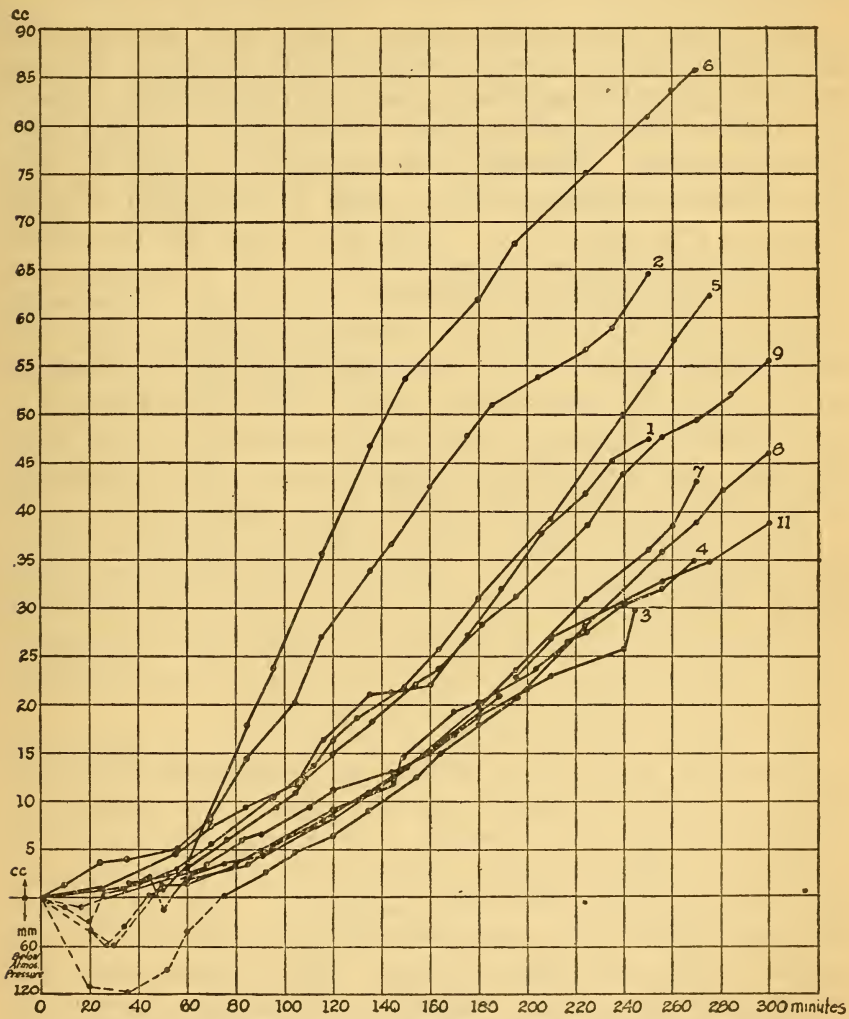

FIG. 9.—*Evolution of gas at 135° C*

tube the mercury was sucked back into the gas-delivery tube to a height of from 10 to 90 mm. After the maximum absorption had been reached the evolution would again commence until there was a constant delivery of gas to the eudiometer. Table 8 gives the ash content of the samples which showed this behavior.

TABLE 8

Ash Content of Samples Showing Reabsorption of Decomposition Gases

Sample	3	4	6	7	8
Ash (per cent)	21.19	20.51	4.97	6.45	4.29

All of these were samples with a considerable percentage of zinc oxide, while the zinc-free articles, such as Nos. 1, 2, 5, and 10, did not show this behavior. There is here an apparent connection between the presence of the basic substance and the absorption of the gases. Mittasch [8] gives one parallel instance in which the addition of ignited marble caused an absorption of gases extending over eight hours. In the article describing his method Mittasch stated that he obtained between 5 and 10 cc of gas from 0.12 g of nitrocellulose in the course of four hours. This would amount to 56–112 cc from 2 g of celluloid containing 70 per cent nitrocellulose, provided the amount of gas liberated is proportional to the amount of nitrocellulose present. The actual amounts of gas evolved by celluloid in this test varied between 30 and 80 cc, showing a rate of evolution of gas of the same order of magnitude as that given by nitrocellulose without any admixtures.

(*f*) *Decomposition above 170° C (338° F)—(Explosion test).*—At temperatures above 170° celluloid articles decompose explosively. The behavior at these temperatures varies somewhat with the sample under test and permits of a classification of the articles, those which withstand the highest temperatures being considered the best as far as danger from fire is concerned.

The form of test used in the determination of the stability of nitrocellulose, and used by Will in the examination of celluloid articles, consists in heating a small sample of the substance in a small glass test tube and noting at what temperature the nitrocellulose or celluloid explodes. This test is open to the objection that the time factor is not taken account of. Thus, for instance, both nitrocellulose and celluloid when kept at 135° for an extended period of time will finally explode. Again, certain samples of celluloid when kept at 170° explode in a definite time; for instance, 10 minutes. It is evident that, assuming the decomposition to have set in at 170°, the explosion temperature registered will depend entirely upon the rate of heating. To overcome this difficulty the explosion tests were made in the following form: [9]

A number of small glass test tubes, 1 cm in diameter and 5 cm long, were kept in an oil bath of constant temperature. A small

[8] Z. angew. Chem., **16**, p. 957; 1903.

[9] H. C. P. Weber, 8th Internat. Cong. Applied Chem., **4**, p. 147, 1912; J. Ind. and Eng. Chem., **5**, p. 641, 1913.

piece of celluloid weighing approximately 0.05 g and compressed to a pellet was dropped into the tube and a stop watch started. A stopper was inserted loosely in the test tube, and the time elapsing until the explosion took place was noted.

This same procedure was carried out with all of the samples at 170°, 180°, 200°, and 220°.

The data from these experiments give a time-temperature explosion curve which yields considerably more accurate information concerning the stability of the sample under question than the simple explosion. The results could be readily duplicated, as shown by the figures given opposite 1A and 1B in Table 9. These particular determinations were made at widely different periods.

TABLE 9

Time of Heating Necessary to Cause Explosive Decomposition of Samples [b]

Sample	220° C (428° F)	200° C (392° F)	190° C (379° F)	180° C (356° F)	170° C (338° F)	Sample	220° C (428° F)	200° C (392° F)	190° C (379° F)	180° C (356° F)	170° C (338° F)
	sec	sec	sec	sec	sec		sec	sec	sec	sec	sec
1A	28	47	.....	60	120	55	40	57	.....	109	n
1B	25	42	.....	60	135	56	45	65	.....	121	135
1	28	47	51	60	120	61	.....	53	.....	50	n
2	42	85	88	100	n	62	.....	22	.....	43	90
3	35	63	65	168	143	63	.....	75	.....	125	n
4	30	50	60	n	n	64	.....	60	.....	115	n
5	24	51	57	n	n	65	.....	43	.....	44	n
6	26	40	60	n	n	66	.....	40	.....	49	138
7	29	75	103	n	n	67	.....	60	.....	69	n
8	28	60	80	85	n	71	.....	28	.....	42	n
9	29	54	90	n	n	77	.....	35	.....	47	n
10	18	45	50	110	n	78	.....	37	.....	50	n
11	50	75	82	n	n	79	.....	35	.....	35	n
12	18	56	.....	165	n	80	.....	41	.....	48	n
21	.....	.....	77	n	n	81	.....	50	.....	52	160
23	.....	.....	46	205	n	101	25	53	.....	95	180
24	.....	.....	64	210	n	102	15	33	.....	83	165
25	.....	.....	73	n	n	103	35	63	.....	115	n
26	.....	.....	92	130	n	104	22	45	.....	90	n
27	.....	.....	75	130	155	105	27	45	.....	n	n
28	.....	.....	51	90	145	111	27	45	.....	117	200
29	.....	.....	40	100	205	114	39	58	.....	127	375
41	48	84		n	n	115	60	95	.....	145	315
42	30	39	.....	86	95	116	50	65	.....	n	n
43	20	49	.....	89	100	119	35	64	.....	160	n
44	40	53	.....	97	n	Collodion cotton	18	56	67	165	870
45	51	79	.....	160	n	Celluloid pyroxylin	9	21	.....	60	170
46	17	35	.....	79	135	Smokeless powder A	23	45	130	195	600
47	34	48	.....	84	n	Smokeless powder B	25	90	.....	130	190
50	27	39	.....	80	n	Black powder	n	n	n	n	n
53	27	51	.....	130	175	Safety matches	60	150	240	340	n
54	45	56	.....	108	n	Parlor matches	480	590	n	n	n

[b] In calculating the averages for 180° and 170° those samples (marked "n") which failed to explode in less than 20 minutes are neglected entirely.

AVERAGES FOR THE VARIOUS CELLULOID SAMPLES

Sample	220° C (428° F)	200° C (392° F)	190° C (379° F)	180° C (356° F)	170° C (338° F)
1–11	31	58	61	98	130
21–29	.....	.....	65	190	172
41–56	35	55	.....	104	140
61–86	.....	48	.....	58	130
101–119	33	52	.....	116	310
Total average	33	53	62	103	163

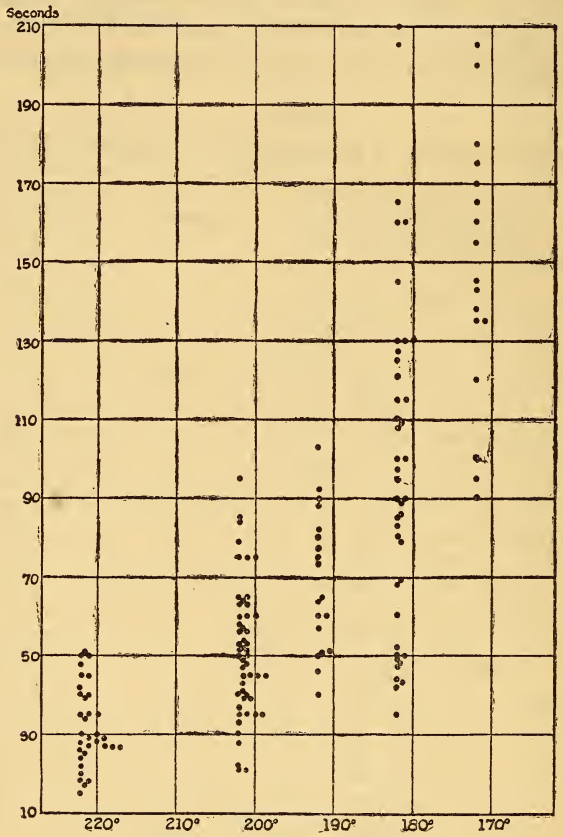

FIG. 10.—*Explosion times of celluloid samples*

The results are given in graphic form in Figs. 10, 11, and 12. Fig. 10 shows the results on samples 1–120. Fig. 11 gives results on various articles for comparison with celluloid. The substances used for comparison are collodion cotton, two samples of smokeless powder, black powder, and safety and parlor matches. The complete results are not given in this plate for lack of space. From Table 9 it may be noted that black powder failed to explode

at or below 220° C, and that parlor matches went off after 480 seconds at 220° C, while nitrocellulose and smokeless powders withstood the temperature of 170° for 190 to 870 seconds.

The curves in Fig. 12 are obtained by averaging the results for various groups of samples and for all of the samples. Thus, 1–11 and 101–119 represent articles obtained directly from American manufacturers and consisting mainly of smooth sheets. Samples 41–56 consisted of toys and various manufactured articles mainly

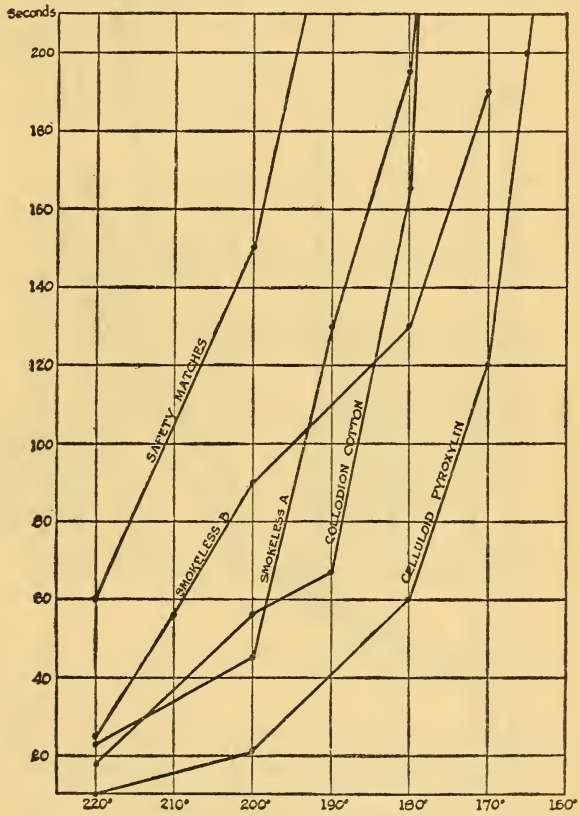

FIG. 11.—*Explosion times of miscellaneous samples*

of American manufacture, while samples 61–81 represent goods manufactured abroad. The fifth curve represents the average values for all of the samples. At the temperatures 170° and 180° a large number of the samples failed to explode, a fact which had of necessity to be neglected in plotting the average times for these temperatures. It may be seen that the various groups of celluloid do not differ greatly in character from each other or from the mean.

(*g*) *Composition of the gases produced by decomposition.*—In order to determine the nature of the decomposition gases formed under normal pressures, the following arrangement was used:

A was a test tube filled with mercury and containing several strips of celluloid. *B* was an inverted bottle also filled with mercury. All connections were filled with mercury. By heating the end of the test tube at *C* decomposition of the celluloid could

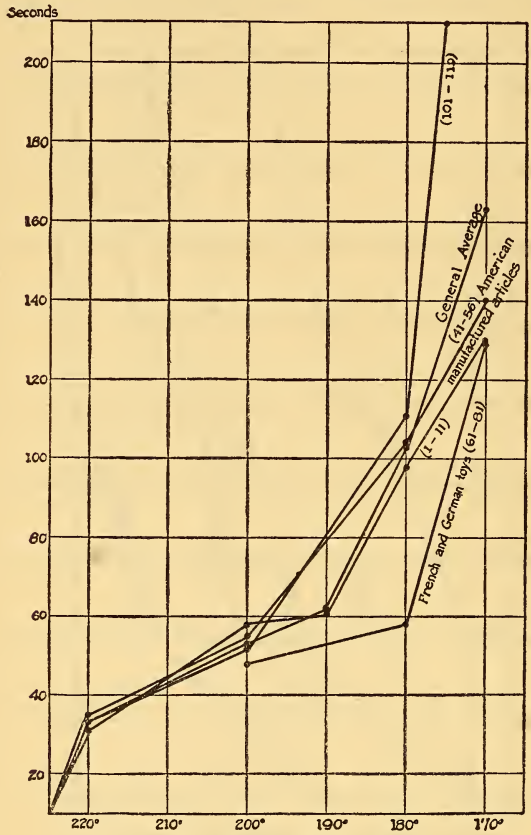

FIG. 12.—*Average explosion times*

be started. The gases generated drove the mercury before them, and decomposition progressed until all of the celluloid had been decomposed. The gases accumulating in *B* were then transferred to a eudiometer and analyzed. The gas was found to contain: NO, 49.3 per cent; CO_2, 16 per cent; CO, 31.7 per cent; and N, 3 per cent.

Will [10] found the composition of the gases obtained by burning celluloid in an iron bomb from which the air had been removed to

[10] Z. angew. Chem., 19, p. 1382; 1906.

be as follows: CO_2, 14.8 per cent; CO, 45.7 per cent; CH_4, 19.4 per cent; H, 10.5 per cent; and N, 9.6 per cent.

In this case the volume of gas obtained from 1 g was 585 cc. The interior space of the bomb was 15 cc. Assuming that the temperature did not rise above 800° during the combustion, a pressure of approximately 160 atmospheres was produced, which accounts for the difference in composition of the gases analyzed by Will and ourselves. In the case of gases obtained by burning celluloid in air, Will obtained: CO_2, 25.8 per cent; CO. 38.4 per

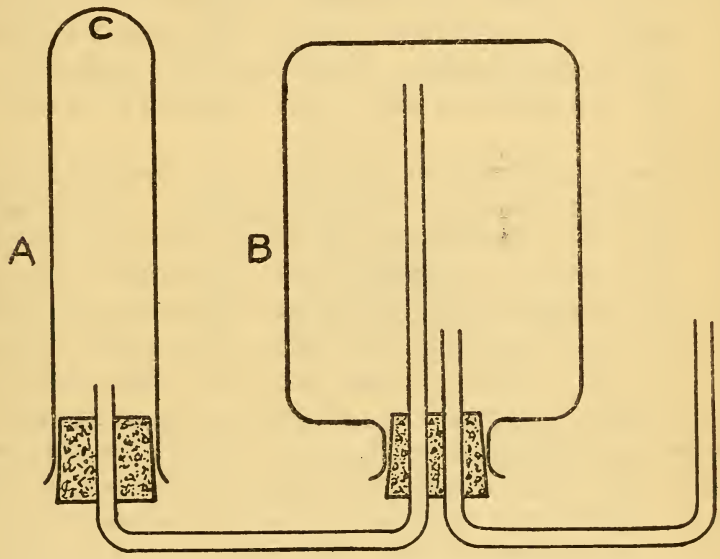

Fig. 13.

cent; CH_4, 5.2 per cent; H, 2.3 per cent; nitric oxides, 23.7 per cent; and N, 4.6 per cent.

Under the conditions in which the gases were produced in the present case combustion was not complete, a great part of the camphor being volatilized with the gases and condensing again, together with liquid and tarry decomposition products. For this reason the gases are extremely inflammable at the moment of formation, so that a test tube containing a piece of celluloid in which decomposition has been started will deliver a burning jet 20 cm or more in height, while if the gases have first been passed through water it is quite difficult to ignite them. The same relation holds as to explosibility.

4. COMBUSTIBILITY

(*a*) *Ignition point.*—There are quite a number of confusing statements made in the literature as to the temperature an object must have in order to cause a piece of celluloid in contact with it to burst into flame. Bronn [11] gives the ignition temperatures of celluloid articles when thrown on a bath of molten antimony as between 355° and 457° and that of ordinary collodion cotton as 130°. In the same article the statement is made that celluloid articles will ignite only when brought in contact with a vigorously burning body, but not a glowing wire or glass rod. Eichengreen [12] cites a number of catastrophes caused by the ignition of celluloid films used in cinematographs. According to this author the rays of the lamp will ignite the film in a few seconds if its motion is stopped.

Experiments performed at this Bureau showed that temperatures between 325° and 650° will cause ignition.[13] The conditions under which the experiments were made influenced the results largely, but there is no question as to the correctness of the limits. The statement might possibly be put that under the most unfavorable conditions for combustion the higher temperature will immediately cause the celluloid to burst into flame, while under conditions favorable to combustion (adequate supply of air and intimate contact) a temperature of 325° will produce the same result. The test was carried out in two forms. In the first test small strips of celluloid were touched with a narrow porcelain tube containing a thermocouple for the measurement of its temperature. The porcelain tube was heated in an electric furnace, the temperature of which was maintained at the temperature of the test. When the porcelain tube had attained the temperature of the heater, it was rapidly withdrawn and touched momentarily with the edge of a piece of celluloid and the fact noted whether the sample burst into flame or not. The tube was returned to the heating furnace and when its temperature had again become constant the procedure was repeated with the next sample, this being continued until all of the samples had been examined at a certain specified temperature. The temperature of the electric heater was then reduced and the samples were examined at the lower temperature. The lowest temperature at which a sample would

[11] Z. angew. Chem., 18, p. 1976; 1905.

[12] Z. angew. Chem., 31, pp. 1354, 1729; 1908.

[13] By ignition in this connection is meant an instantaneous production of flame, without intervening slow decompositions.

instantaneously burst into flame, under these conditions, was considered the ignition temperature.

The results obtained in this manner are given in Table 10.

TABLE 10

Ignition Temperatures of Samples in Contact with Porcelain Tube

Sample	Temperature		Sample	Temperature	
	Deg. C	Deg. F		Deg. C	Deg. F
1	600	1112	48	642	1188
2	613	1135	49	618	1144
3	594	1101	63	588	1090
4	594	1101	64	588	1090
5	558	1036	65	588	1090
6	586	1087	67	606	1123
7	552	1026	71	583	1081
8	570	1058	79	583	1081
9	570	1058	80	583	1081
10	552	1026	81	630	1166
11	586	1087	Smokeless powder	300	572
41	618	1144	Black powder	440	824
44	596	1105	Cotton wool	900	1652
45	618	1144	Nitrocellulose (collodion)	300	572
47	648	1198			

The second series of tests was made by dropping small pieces of celluloid on molten lead. The details of the manipulation were as follows: The lead was contained in a piece of iron pipe closed at one end and capable of holding about 250 cc. This was contained in a second vessel and surrounded by iron filings and the whole apparatus heated by a gas flame. With this arrangement the temperature could be maintained very constant. Temperature was read by means of a thermocouple contained in a small porcelain tube and plunged into the center of the lead bath. A small piece of celluloid not more than 3 or 4 mm in diameter and weighing but a small fraction of a gram was dropped on the clean surface of the molten lead. The lowest temperature at which the sample immediately burst into flame was taken as the ignition point of the celluloid. The results are given in Table 11.

TABLE 11

Ignition Temperatures of Samples in Contact with Molten Lead

Sample	Temperature		Sample	Temperature	
	Deg. C	Deg. F		Deg. C	Deg. F
1	433	811	9	433	811
2	459	858	10	446	835
3	495	923	101	433	811
4	495	923	102	433	811
5	433	811	103	495	923
6	433	811	104	433	811
7	433	811	114	523	973
8	446	835	119	471	880

As will be noted, the temperatures obtained in this manner are considerably lower than with the preceding test. A part of the difference may be explained by the fact that in the second method the sample is surrounded by a highly heated atmosphere, while in the first the greater part of the sample was at normal temperature and only that small portion in direct contact with the hot rod was heated. In both cases the matter is complicated to a certain extent by the fact that the vapors from the decomposition, when mixed with air, ignited at a decidedly lower temperature than the substance itself; that is, the ignition temperature of the vapors depends largely on the ratio of air and vapor, the ignition temperature of the mixture some distance away from the sample being lower than that in its immediate neighborhood. For this reason the test was made with small samples, so as to obviate as much as possible the accumulation of explosive vapors. The ignition point for this series was taken as that at which the substance bursts into flame instantaneously, before opportunity for the formation of an explosive gas mixture has been given. The vapors from the decomposing celluloid were repeatedly ignited at 425° C. The lowest temperature observed at which ignition took place was 380° C, or considerably below the melting point of lead.

(*b*) *Rate of combustion.*—To determine the rate of combustion, samples of celluloid in strips were compared with fat pine wood and with poplar of the same dimensions. For comparison with the very thinnest samples of celluloid ordinary writing paper was used.

The tests were made with strips horizontal, vertical, ignited from below, and vertical, ignited from above. The sample was ignited at one end and the time taken in burning 10 cm was noted with a stop watch. The results are given in centimeters per second; e. g., 0.08 means that the flame progressed 0.08 cm every second.

TABLE 12

Rate of Burning of Celluloid Compared with Wood and Paper

[In centimeters per second]

Sample	Horizontal	Vertical, ignited from below	Vertical, ignited from above
CELLULOID STRIPS 2-2.1 MM THICK, 5 MM WIDE, COMPARED WITH WOOD			
Poplar	0.08	0.31	(a)
Pine	.04	.22	(a)
Celluloid No. 2	.56	1.67	0.25
Celluloid No. 11	.37	1.67	.18
CELLULOID ROD 13 MM SQUARE CROSS SECTION COMPARED WITH WOOD			
Celluloid	0.25	0.33	0.17
Pine [b]			
CELLULOID, 0.5 MM THICK, 1 CM WIDE, COMPARED WITH WOOD			
Poplar shavings	0.40	0.77	0.14
Celluloid No. 3	.67	2.00	.48
Celluloid No. 4	.83	2.00	.48
CELLULOID, 0.24 MM THICK, 1 CM WIDE, COMPARED WITH PAPER			
Paper	0.21	0.83	0.09
Celluloid No. 6	1.00	5.00	1.00
Celluloid No. 7	1.00	5.00	1.00
Celluloid No. 1	.77	4.54	.67
Celluloid No. 8	1.00	4.54	.90
Celluloid No. 9	1.00	4.10	1.00
Celluloid No. 5	1.67	6.30	1.43
Celluloid No. 10	.83	4.10	.72
Celluloid No. 101	.77	2.10	.53
Celluloid No. 102	1.56	5.00	1.50
Celluloid No. 103	.71	2.00	.42
Celluloid No. 104	1.35	5.00	1.28

[a] Went out several times. [b] Would not burn continuously.

The results show that the rate of progression of flame for the celluloid samples is from two to fifteen times as rapid as for thin sheets of paper or for strips of wood of the same thickness and width. A solid piece of celluloid 13 mm square in cross section burned with practically the same rapidity as the smaller samples, while the piece of wood of the same dimensions repeatedly went out, so that no numerical comparison could be made.

(*c*) *Effect of continued heating below ignition point.*—In the Chemiker-Zeitung [14] of 1905 there is an extended discussion of the

[14] Chem.-Ztg., 29, pp. 85, 94, 127, 128, 144, 165, 187, 188, 203, 1905.

liability of celluloid to spontaneous combustion, cases being cited of celluloid combs while being worn bursting into flame from the radiant heat of stoves. The decomposition of nitrocellulose is autocatalytic, and once having set in the temperature of the mass will rise to the dangerous point, provided the radiation of heat away from the decomposing substance is prevented. To show this the following experiments were carried out:

Two sticks of celluloid from the same sample were taken. The sticks were 13 mm square in cross section and about 50 mm long. A hole was drilled in each to receive a thermometer. One sample was surrounded by loosely packed cotton wool, the other was left unwrapped. Both samples were inserted in a Victor Meyer bath, the temperature of which was kept constant by boiling amyl acetate. Three thermometers gave the temperatures of the unwrapped and wrapped samples and of the bath. Table 13 gives the temperature of the bath, of the unwrapped sample and of the wrapped sample after various periods, calculated from the time when the heating was commenced.

TABLE 13

Temperatures Reached by Samples Heated in Victor Meyer Bath

EXPERIMENT A

Total time of heating	Bath	Unwrapped sample	Wrapped sample
h m	° C	° C	° C
2 25	136	139	141
2 45	136	139	145
3 00	135.5	139	148
3 05	136	139	150
3 08	136	139	153
3 10	136	139	155
3 12	136	139	[a]158
EXPERIMENT B			
– 55	134.5	137	124
2 30	134	138	134.5
2 38	134	138	136
2 53	134	138	138
3 07	134	138	138.5
4 30	134	138	140
4 37	134	138	142
4 43	134	138	143
4 45	134	[b] 138	143.5

[a] Sample suddenly went up in smoke.
[b] Sample suddenly went off.

In these two cases the temperature of the unwrapped sample was several degrees above that of the constant temperature bath, but after having reached a certain point where the radiation loss was equal to the heat evolved by decomposition it remained constant. The wrapped samples, however, steadily rose in temperature, this rise increasing rapidly until the point was reached where the decomposition proceeded explosively. In both cases the cotton wrapping was charred and found to be glowing, while in one instance the vapors took fire.

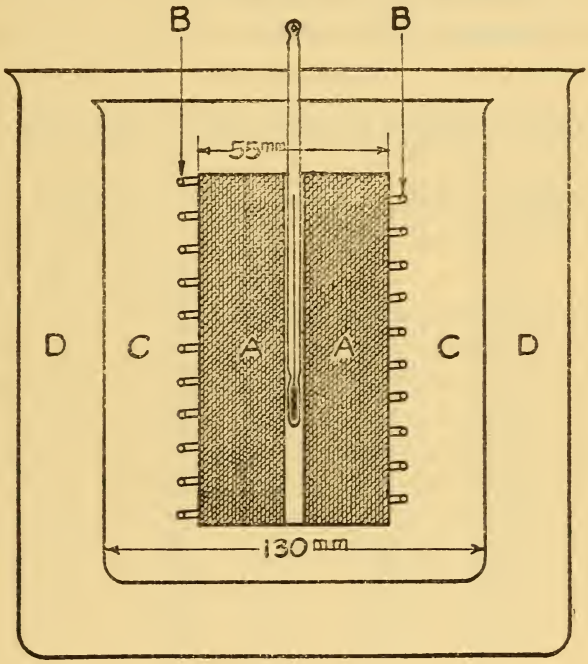

FIG. 14.

In the same manner experiments carried out by keeping two sticks of celluloid, one wrapped and the other unwrapped, at a constant temperature of about 97° in a Victor Meyer bath (the boiling liquid being water) failed to give an increase of temperature due to decomposition.

In the next series of tests a lower initial temperature was chosen, using the arrangement shown in Fig. 14.

Three hundred grams of celluloid, in sheets, was rolled into a cylinder, *A*, with an opening in the center large enough to admit a thermometer. Surrounding the cylinder was a coil of lead tubing, *B*, and around this a layer of cotton wool, *C*, was loosely

packed. The whole arrangement was contained in a beaker, *D*, containing boiling water in a number of experiments and cotton wool in others. The steam flowed through the lead coil surrounding the celluloid.

The temperatures observed in three tests are shown in Table 14, the periods of time being calculated from the moment steam was turned on. The material in each case was a composite sample, composed as follows:

Test No. 1: Samples 1, 4, 5, 6, 7, 8, 9, and 10.
Test No. 2: Samples 2, 4, 5, 6, 7, and 8.
Test No. 3: Samples 1, 3, 9, and 10.

TABLE 14

Rise in Temperature of Samples Heated by Steam Coil

Time of heating.	Test No. 1.	Time of heating.	Test No. 2.	Test No. 3.
h m	° C	h m	° C	° C
1 30	100	10	103.5	97
2 30	102	1 30	105	95
3 30	103	2 00	105	..
4 15	104	2 45	108	100
5 15	104	2 55	109	102
5 30	107	3 15	111	102
6 00	110	4 15	115	110
6 10	112	4 40	116	112
6 37	114	5 10	116.5	112
6 50	120	5 30	119.5	112
7 07	123	5 40	121	113
7 10	125	6 00	126	116
7 15	127	6 15	127	119
7 43	131	6 30	128	123
7 50	133	7 00	129.5	129
8 00	138	7 15	130	132
		7 25	131	134.5
		7 35	132	138
		7 40	132.5	140
		7 42	133	141
		7 45	134	144
		7 50	135	147
		7 52	136	150
		7 54	...	156
		7 56	136.5	162

Subsequent to the observations shown in Table 14, the behavior was as follows:

In test No. 1, 30 minutes after the last observation, the sample suddenly decomposed, filling the room with such a large quantity of dense, biting fumes that it was impossible to remain in it. Upon examining the contents after the room had cleared, it was

found that there was nothing left of the celluloid but a black porous ash. The glass containing the sample had been cracked, allowing the water, which surrounded the glass in this test, to enter and extinguish the celluloid. That part of the cotton packing which had not been wet by the incoming water was smouldering and burst into flame upon opening it to the air.

Test No. 2 had reached a temperature of 138° one-half hour after the last observation. The steam was thereupon turned off. Five minutes later the thermometer showed 139° and immediately decomposition set in. A moment afterward the gases exploded under the hood in which the test was being made and burned with a sheet of flame about 2 feet high. After the flame had gone out it was found that the lead coil had been melted down completely. The packing of the outside beaker in this test was cotton.

Test No. 3 exploded five minutes after the last observation, giving the usual dense fumes. The cotton packing was glowing and burst into flame on opening and blowing upon it. The outer packing in this case was sand.

Two more tests were made with articles from a source different from those used in the preceding experiments. In one experiment samples of plain sheets and in the other toys which had been crushed flat and wrapped in a package similar to the preceding were heated. Both of these samples exploded as the previous ones had done, the decomposition products in one of the experiments bursting into flame. In all of these instances the steam entered the coil somewhat above atmospheric pressure. In the last two cases an arrangement for measuring the temperature of the incoming steam was inserted before the celluloid samples, the temperature remaining between 110° and 120°.

In an experiment made with the same arrangement, but using ordinary sawdust as the packing material, the samples did not explode even after very prolonged heating. When opened, however, the goods were found to be charred and otherwise badly decomposed.

(*d*) *Effect of heat produced mechanically.*—The fact that celluloid may be ignited by friction, such as sawing, etc., is known. As an illustration of this a cylinder of celluloid sheets of which it was desired to saw off the end ignited during the operation. After a cut about 5 mm in depth had been made by the circular saw rapid decomposition set in. The roll was at once thrown under running water, but decomposition progressed until the roll was completely covered with water. The fumes filled a work-

shop 50 feet square so full of dense biting fumes that it had to be vacated. Upon weighing the sample afterwards it had lost about 100 g.

(*e*) *Extinguishing burning celluloid.*—The behavior of the substance under these conditions suggested the question as to whether conditions might arise in which it would be impossible to extinguish burning celluloid with water. To decide this a small box, 5 by 5 by 10 cm, made of wood 3 mm in thickness, was used. This was filled with strips of celluloid just wide enough to fit into the box. Every few strips were separated by tissue paper, the whole being made to approach the ordinary arrangement in packing. The box could be closed by a sliding lid. When everything was ready, a glass rod was heated in a flame and the celluloid was touched with it, thus starting off the decomposition without causing the material to burst into flame. The lid of the box was closed and the whole arrangement plunged into a vessel of water and held under the water. Decomposition proceeded just as in the open air, large volumes of fumes being given off, which prevented access of the water to the celluloid until practically all of it had been burned up.

VI. CONCLUSIONS

The following conclusions, while not all new, are all justified by the results of our experimental work. Many of them are expressed graphically in Fig. 15.

1. Celluloid (using the term in its popular sense to include the pyroxylin plastics in general) does not differ essentially from nitrocellulose. The difference is one of degree and not of character. Nitrocellulose exists and reacts in celluloid as such; that is, as a solution of nitrocellulose in camphor or other solvent present, rather than as a new chemical compound. The admixture up to 20 per cent of zinc oxide does not decrease the rate of decomposition of the nitrocellulose in celluloid, the results seeming rather to show that there is an increase.

2. The decomposition of nitrocellulose in celluloid commences in the neighborhood of 100° C. Above this temperature the heat of decomposition may raise the temperature of the mass to the ignition point, if loss of heat by radiation is prevented.

3. Above 170° the decomposition of celluloid takes place with explosive violence, as with nitrocellulose.

4. The rate of combustion is five to ten times that of poplar, pine, or paper of the same dimensions and under the same conditions.

5. Celluloid articles may be ignited by momentary contact with bodies having a temperature of 430° or above, i. e., temperatures below visible red heat.

6. In spite of wide differences between individual samples, no essential differences were found between the celluloids of American manufacture, nor between articles of American and foreign manufacture, nor between manufactured and unmanufactured articles.

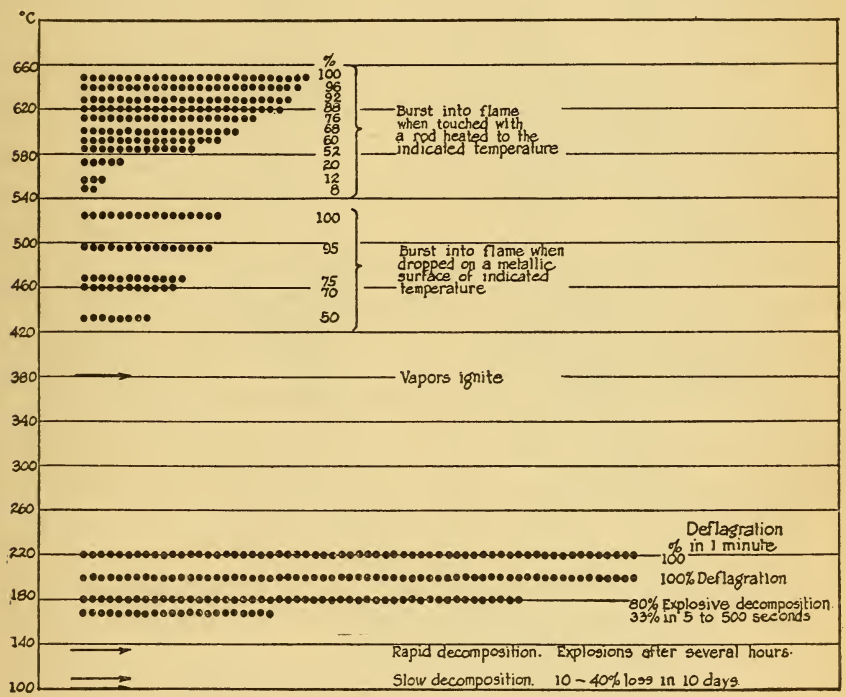

FIG. 15.—*Behavior of celluloid at various temperatures*

7. The general qualities of celluloid as to stability may be best expressed by a time-temperature curve, taking the time necessary for exploding small samples at several temperatures, say, 170°, 180°, 200°, and 220°.

8. The vapors evolved by decomposition are poisonous and extremely combustible and may be ignited by the heat of decomposition of the celluloid itself.

9. The decomposition of celluloid is autocatalytic, and while not necessarily explosive may readily approach that condition as a limit.

WASHINGTON, February 5, 1917.

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